

Modeling and Measurement of Aryl Phosphate Ester Vapor Pressures at 50°C

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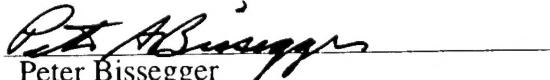
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1. Introduction

Satellite and spacecraft mission lifetimes have progressively grown longer with time. High vapor pressure, mineral oil lubricants that were used on previous missions may not be adequate for longer-lifetime missions. Lower vapor pressure, synthetic lubricants are replacing mineral oils on satellite moving mechanical assemblies (MMAs) in many applications. Not only is it important that the oils remain in the contacting areas of the MMAs for the duration of the application, it is also important that the additives formulated in the lubricants remain. New additives with lower vapor pressures are being used with the low vapor pressure synthetic oils.

To assess adequately the evaporative loss of lubricants and additives from spacecraft MMAs, it is necessary to use reasonably accurate vapor pressure vs temperature data in the loss calculations. Unfortunately, these data are not always available in the literature, and the data that are available are not always dependable at lower temperatures (generally 0 to 50°C). For example, vapor pressure data exist for a number of pertinent compounds at high temperatures, 150–450°C.¹ Extrapolating these data to the lower temperatures of interest makes use of the Clausius-Clapeyron relationship:

$$\ln P = \left(-\frac{\Delta H_{vap}}{RT} \right) + \text{const.}, \quad (1)$$

where, P is the vapor pressure, H_{vap} is the enthalpy of vaporization, R is the gas constant, and T is the absolute temperature in K. The tacit assumption of this procedure is that the relationship is linear over large temperature and vapor pressure ranges. The fact is that log vapor pressure vs 1/T behavior is generally not linear over these large ranges.^{2,3} The assumption that the extrapolated vapor pressures can be used for conservative calculations implies that the deviation from linearity is not large, and that the vapor pressures are modestly overestimated. We have shown that extrapolation of high-temperature hydrocarbon vapor pressure data to lower temperatures can introduce errors as large as 2 orders of magnitude.⁴

With this in mind, in the absence of vapor pressure data for many compounds at lower temperatures, we have derived vapor pressures from extrapolated data and have performed oil-loss calculations for MMAs on a number of satellite systems. For example, the synthetic hydrocarbon oil, trialkylated cyclopentane, is commercially available with an antiwear additive mixture that is composed of four aryl phosphate ester components. In the past, we have estimated the vapor pressures of these esters by extrapolating high-temperature data for two different phosphate esters using the assumption (which has been shown to be true for hydrocarbons) that for a series of chemically related compounds (same functional group), the log vapor pressure scales with the molecular weight.⁴ These vapor pressures, along with some hardware tests, were used to show that the additives would not cause problems due to vapor-phase transport. We considered the calculations to be conservative because we suspected that the actual vapor pressures were lower than the estimated values. In this report, we present experiments in which the vapor pressures of these aryl phosphate ester additives are determined at a more typical operational temperature, 50°C.

2. Experimental

2.1 Materials

The additives used in the experiments were tricresyl phosphate (TCP) from William F. Nye, Inc. and FMC Corporation and the four-component, aryl phosphate ester mixture from William F. Nye, Inc. The four components in the mixture are triphenyl phosphate, t-butylphenyldiphenyl phosphate, di-(t-butylphenyl)phenyl phosphate, and tri-(t-butylphenyl) phosphate. The additives were used as received. The TCP samples are both mixtures. With ortho, meta, and para methyl substitution possible, there are 27 possible isomers. However, the ortho isomers are carcinogenic and are not present in large concentrations. Thus, the mixtures are primarily composed of eight possible meta and para methyl isomers. Figure 1 shows supercritical fluid chromatograms for the two samples. There are at least three isomers that are major components in the mixtures. We will show in the Discussion section that the vapor pressures of the mixtures are not affected by the composition.

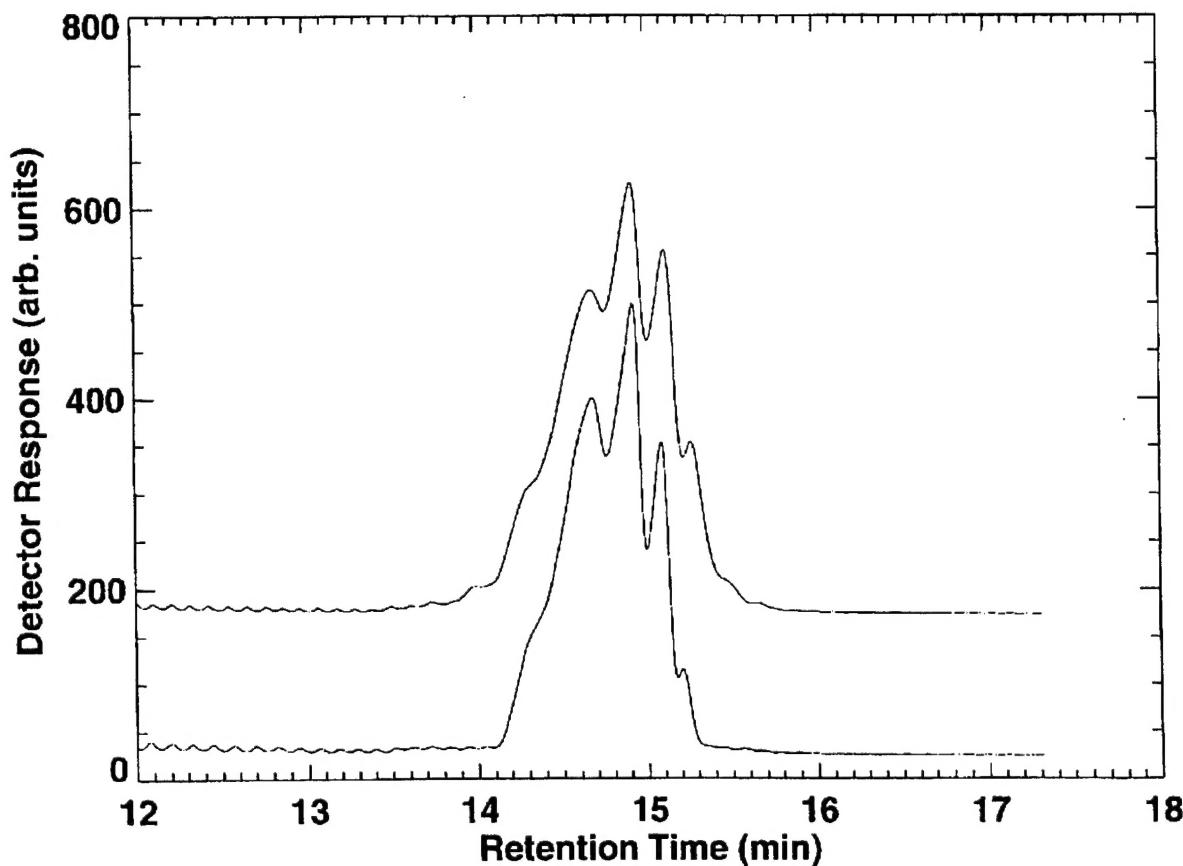


Figure 1. SFC chromatograms of TCP samples (arbitrary ordinate offset).

2.2 Method and Apparatus

The experimental approach chosen was non-equilibrium weight loss measurement under vacuum conditions. Under the conditions that the evaporation coefficient is 1, and the return rate of gas molecules to the surface is effectively zero because of the large mean-free path under vacuum, it has been shown that the vapor pressure can be calculated from the mass loss rate.⁵ The accommodation coefficient, α , and, thus, the evaporation coefficient, has been shown to be 1 for aryl phosphate esters.⁶ Static methods, such as the isoteniscope method, were not chosen because we were interested in the rate of mass loss of additives. Static methods are sensitive to small concentrations of volatile impurities, which are not significant in the mass loss method. Effusion methods were also rejected because of the long times required for the experiments. At the experimental temperature, 50°C, thermal decomposition of the samples has been shown not to be a concern, either in the liquid⁷ or the vapor phase.^{8,9}

The loss rates of the additives were measured using the apparatus shown in Figure 2. (The apparatus and procedure have been described in a previous publication.⁴) It consists of 16 separate, removable

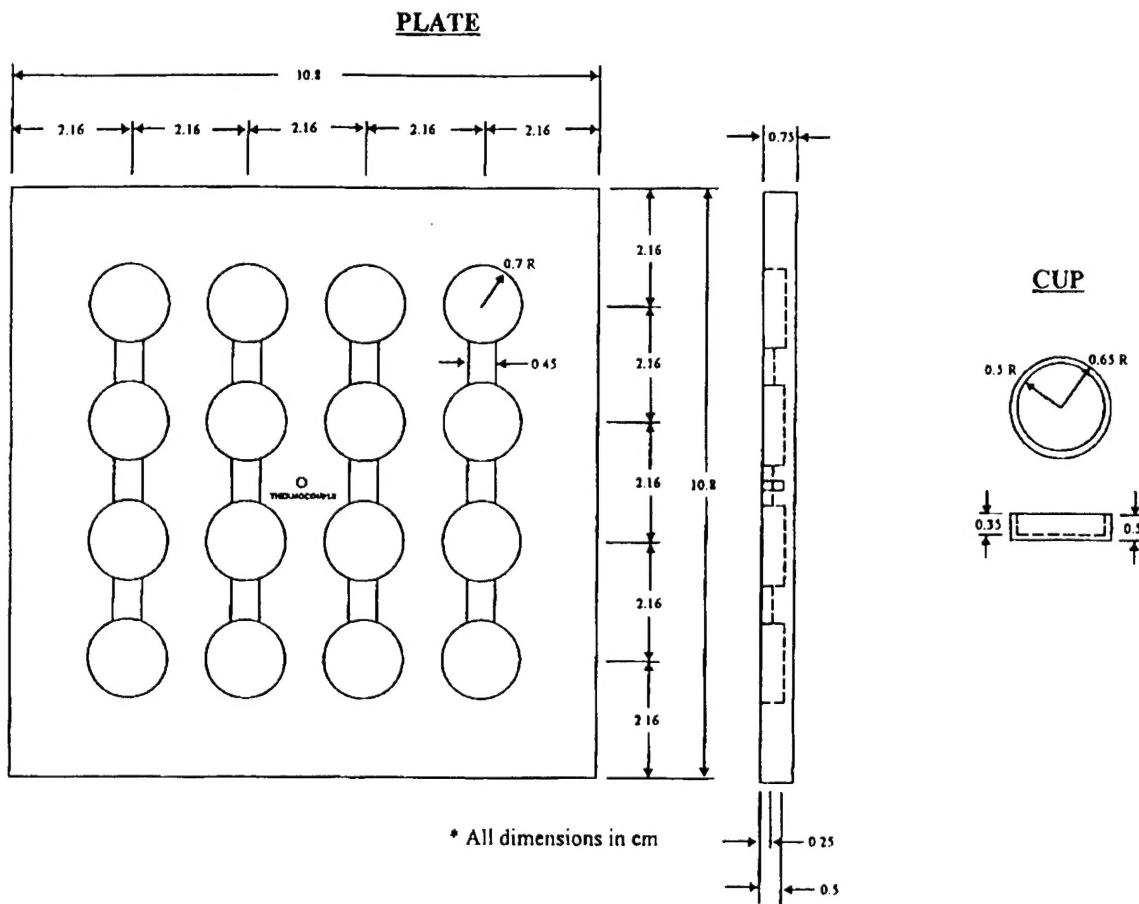


Figure 2. Oil evaporation apparatus.

aluminum cups that are each 1 cm internal diameter (sample surface area = 0.8 cm²). The aluminum cups fit into holes in an aluminum base plate that is heated by a film heater. The temperature is measured and regulated using a thermocouple in the center of the base plate. The position-to-position variation in temperature has been determined to be $\pm 1^{\circ}\text{C}$. The apparatus is housed in a bell jar that is pumped with a turbomolecular pump. Background pressures were $<1 \times 10^{-4}$ Pa during the experiment, ensuring that free molecular flow conditions were maintained. The pressure was reduced slowly enough that no bubbling or frothing of the samples was observed. Since the measured vapor pressures are so low (3×10^{-4} Pa; see below), free molecular flow conditions obtain even close to the cups.

2.3 Procedure

Samples of approximately 50-mg of each additive were placed in the preweighed aluminum cups. Several samples of each additive were used. The cups were weighed again to determine sample size. They were then placed in the holes in the aluminum plate and installed in the bell jar. The system was evacuated and maintained at low pressure and room temperature for ~24 h. (A small amount of the most volatile of the aryl phosphate mixture components will be lost during the initial 24-h period. This will be shown to be insignificant later.) After the 24-h period, the system was heated and maintained at the test temperature, 50°C, until a measurement was required. At that time, the system was vented, the apparatus cooled to room temperature, and the individual sample cups weighed. The samples were placed back in the bell jar, pumped for 24 h at room temperature, and then heated to the test temperature. This process was repeated to the end of the test. The effect of moisture absorption while the samples are exposed to atmosphere prior to weighing is not considered to be significant. The time of exposure is short, limiting the amount of water that could be absorbed, and is approximately the same for each weighing. If the amount of moisture uptake was constant, then the results would not be affected because we use the difference in weight from the initial weight as a measure of mass loss. If there is significant variability in the absorption of water, this would be manifested as large scatter in the data. This will be shown not to be the case.

3. Results and Discussion

3.1 Tricresyl Phosphate (TCP)

Mass loss vs time data for the TCP from both suppliers are given in Figure 3. Three samples from each product were used. The data for each sample are represented by a different symbol in the figure. There is a good correlation of data for all the samples, and the data for the two sources are essentially the same. The composite slope for all data was calculated. This is represented by the solid line in the figure. The Langmuir equation is expressed as

$$P = 2.29 \times 10^3 \left(\frac{T}{MW} \right)^{0.5} G, \quad (2)$$

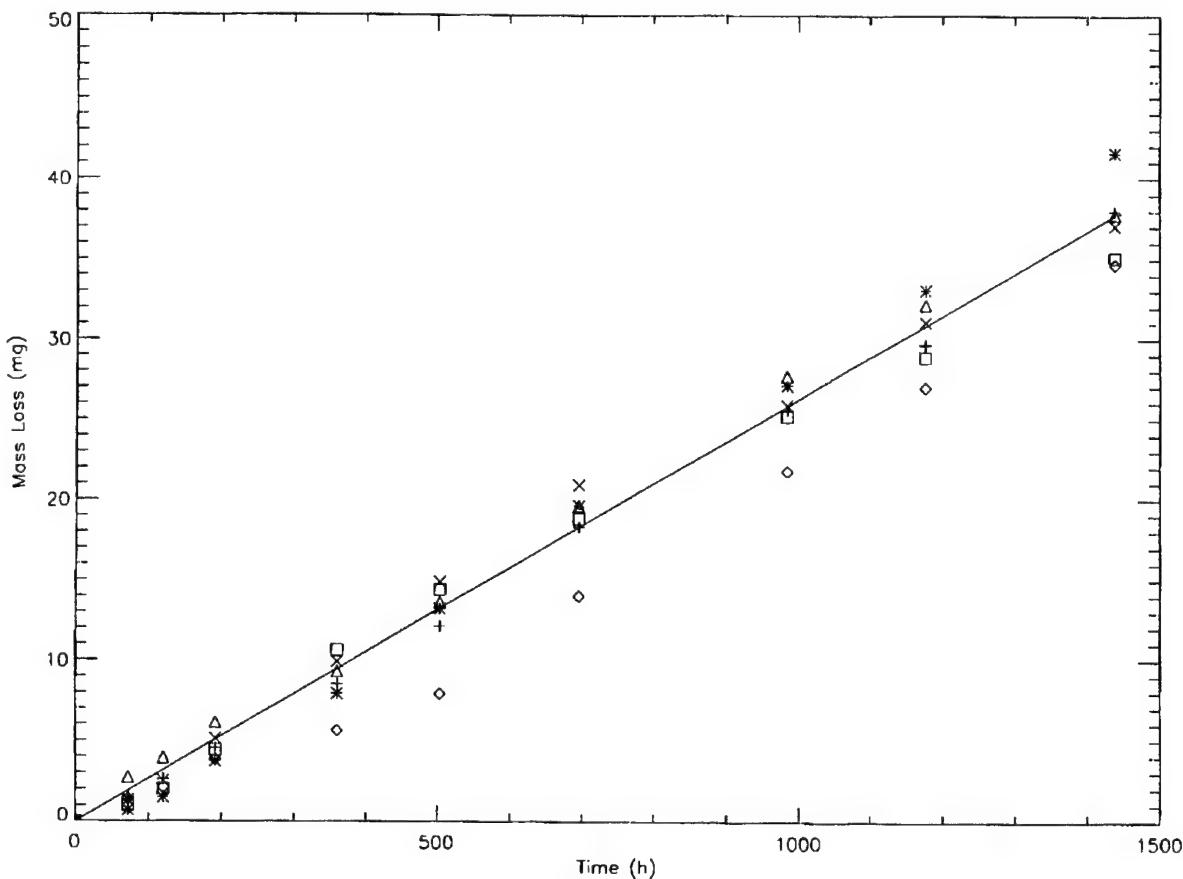


Figure 3. Mass loss vs time data for TCP at 50°C. The \square , \diamond , \triangle symbols are for the TCP sample from one supplier, the $*$, \times , and $+$ symbols are for the TCP sample from the other supplier, and the solid line is a fit to all the data.

where P is the vapor pressure in Pa, T is the temperature in Kelvin (= 323 K), MW is the molecular weight ($= 368 \text{ g mol}^{-1}$), and G is the loss rate in $\text{g cm}^{-2} \text{ s}^{-1}$. This equation was used to calculate the vapor pressure for the TCP. The area used to calculate G was the surface area of the top of the liquid in the cup (0.8 cm^2). A small amount of material could migrate to the inner walls of the cup by surface diffusion or vapor deposition. No bulk films of liquid are expected on the sides of the cups because of the forces due to the meniscus at the surface/wall interface.¹⁰ Thin films of polar molecules have desorption rates up to 3 orders of magnitude smaller than the bulk material,¹¹ so the effects of any thin films on the cup sides would be small and are ignored. The geometry of the cups led to a Clausing factor¹² of 0.77. Rate loss rates were divided by this factor to arrive at the appropriate vapor pressure. The calculated vapor pressure is $2.6 \times 10^{-5} \text{ Pa}$ at 50°C. (Each 24-h pump-down period at room temperature after weight measurements resulted in a calculated TCP loss of $<0.02 \text{ mg}$, which is insignificant.)

Figure 4 gives the data for one sample from each product, offset on the ordinate for comparison purposes. The data are clearly linear up to >70% mass loss, with little deviation of the data from the least-squares fits shown in the figure. (The small difference in slope between the two is consistent with small temperature differences in sample position in the apparatus.) This result shows that the vapor pressure of the mixture is insensitive to the composition, and that the vapor pressures of the

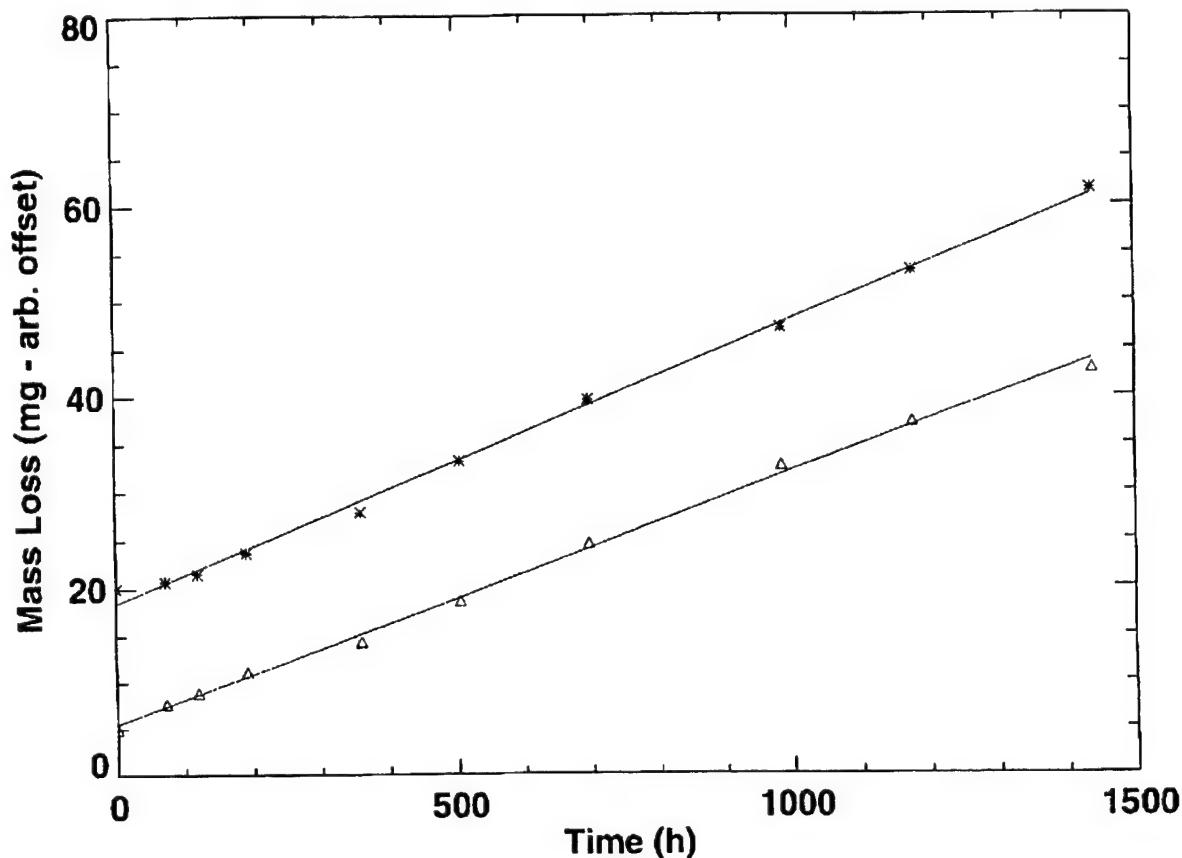


Figure 4. Mass loss vs time data for TCP, one sample from each supplier.
The ordinate offset in the data is for comparison purposes.

components are very similar, grouped within a factor of 2. It has been shown that the vapor pressures of tri-p-cresyl phosphate and tri-m-cresyl phosphate are very similar.⁶ Small concentrations of volatile components are inconsequential in our experiments. The data also show that moisture absorption does not affect the results and that decomposition reactions are not significant. If significant decomposition was occurring, such as reaction with the aluminum pans, the plots would not be linear, except under the extraordinary circumstance that the decomposition products had exactly the same vapor pressures as the sample components, which is very unlikely and can be rejected.

The calculated value for the vapor pressure of TCP from extrapolating literature data¹ from very high temperatures (155–313°C) leads to a value of 4.7×10^{-2} Pa at 50°C. The vapor pressure determined in our experiments is a factor of ~1800 less than that extrapolated from high-temperature data. The implications of this finding are that the Clausius-Clapeyron relationship is not linear, and the absolute value of the slope (ΔH_{vap}) increases with decreasing temperature (curve is concave downward). Linear Clausius-Clapeyron behavior would occur if ΔH_{vap} were constant over the temperature range of the extrapolation. ΔH_{vap} depends upon the heat capacity, which has been shown to be a function of temperature for organic compounds,¹³ and has been shown to vary with temperature for aryl phosphates.¹⁴ Extrapolations of vapor pressure data can only be acceptable over limited temperature ranges.² Vapor pressure data for TCP in the temperature range 107–147°C taken from reference 15, as well as our value at 50°C, are shown in Figure 5. Modest downward curvature of the plot

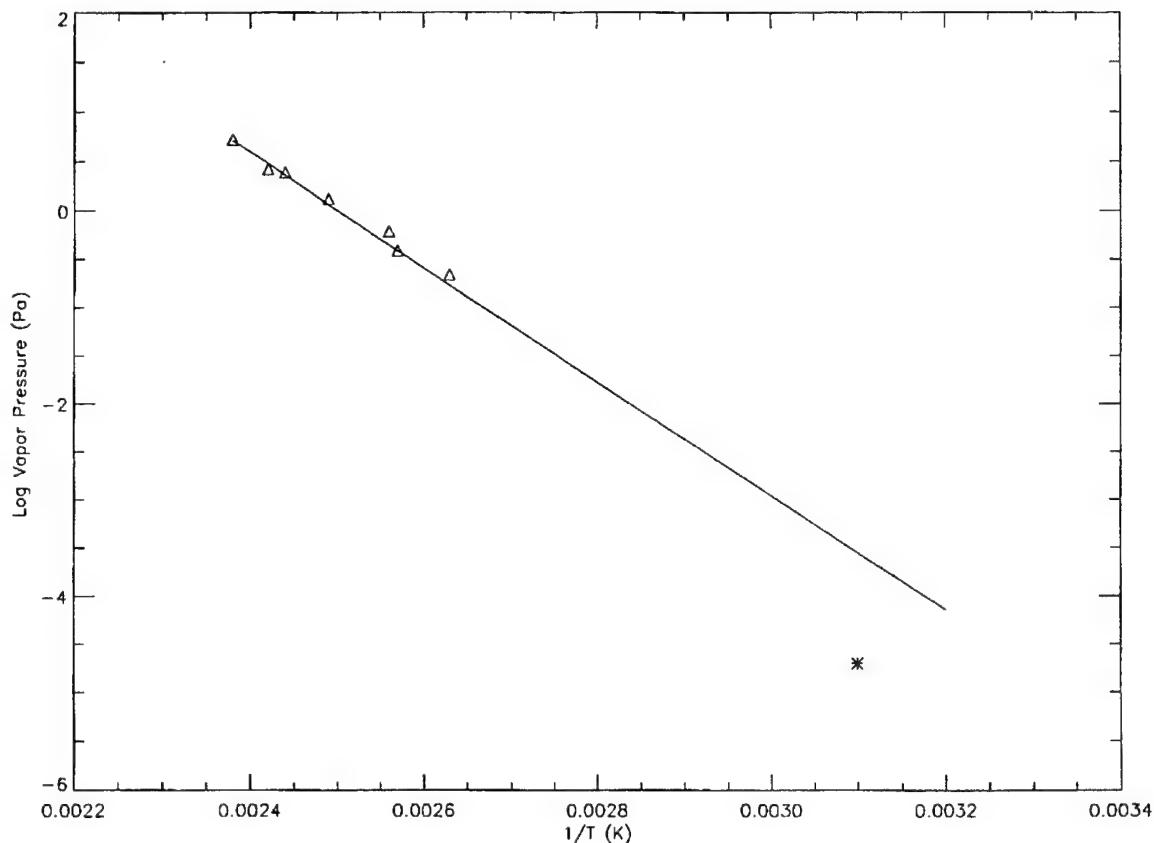


Figure 5. TCP vapor pressure vs 1/T. The Δ symbol is for data from ref. 15, the * symbol is the data point from this work, and the line is the linear extrapolation of the data from ref. 15.

would be consistent with our vapor pressure value. Curved Clausius-Clapeyron behavior has been invoked to explain the large difference between vapor pressures measured at high and ambient temperatures for hydrocarbons,⁴ and has been observed for dibutyl phthalate esters.¹⁵ A value of 6.1×10^{-6} Pa at 25°C was reported using a chromatographic retention time approach.¹⁶ This value is more consistent with linear extrapolation of higher-temperature data. Since downward curvature is expected, we believe this value is too high by at least an order of magnitude.

In a practical sense, using the extrapolated high-temperature vapor pressure data would drastically overestimate the loss of TCP from lubricants. Since most lubricants are formulated with 1% TCP, using Raoult's law (the loss rate of a component is proportional to its mole fraction) and our experimentally determined vapor pressure leads to an initial TCP loss rate at 50°C of 2.5×10^{-7} g cm⁻² h⁻¹, which is very low. (The loss rate would decrease with decreasing TCP concentration.)

3.2 Aryl Phosphate Ester Mixture

Percent additive loss vs time data for four samples are given in Figure 6. It is clear that the loss rates are changing as a function of time due to loss of the more volatile components. Initial rates can be calculated from the data. However, this does not yield vapor pressures for the individual components. We elected to model the loss and derive vapor pressures by fitting the data.

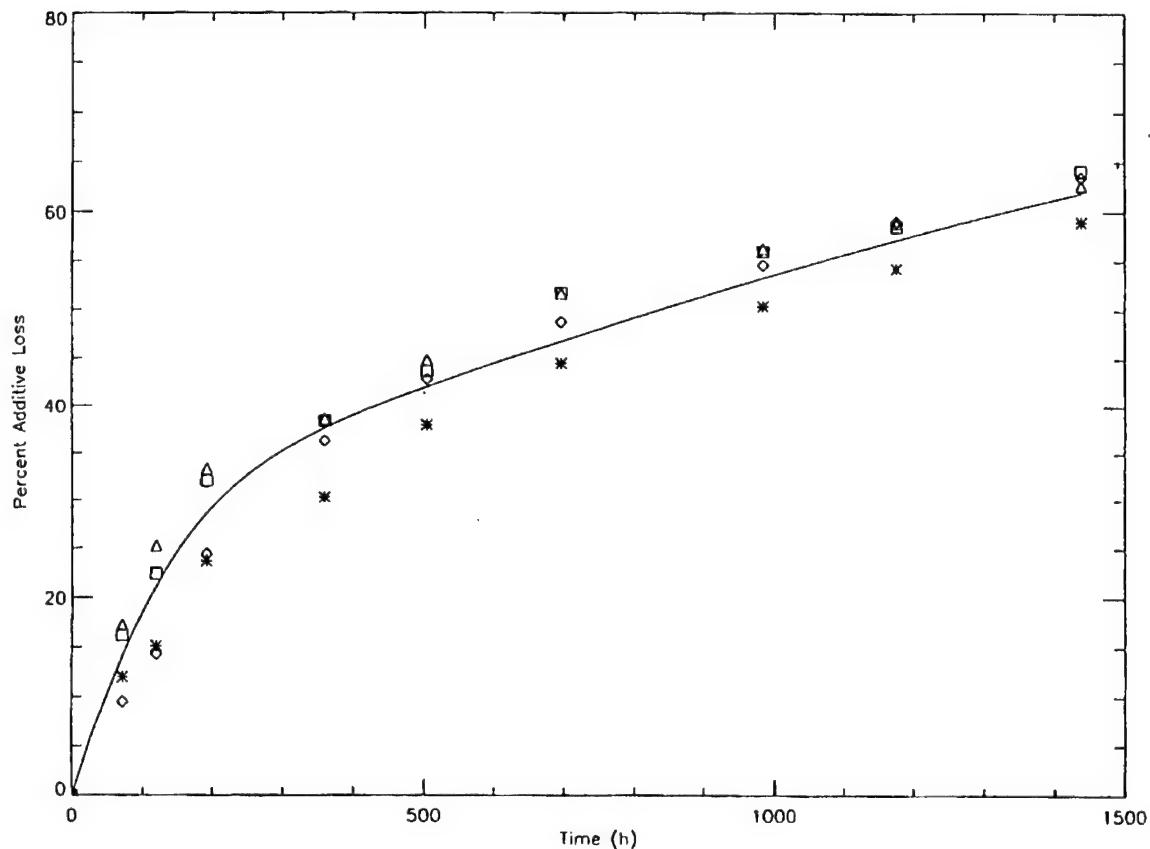


Figure 6. Percent oil loss vs time data for aryl phosphate ester mixture at 50°C. The symbols represent individual sample data; the line is the fit obtained from the model.

3.2.1 The Model

A computer program was written in IDL® (Interactive Data Language). In the program, the component vapor pressures, mass fractions, and evaporation time periods are varied to obtain the best fit to the empirical data. The other component parameters are either known (molecular weights) or are obtained from the vapor pressures and mass fractions (mole fractions and loss rates for each of the four components). Thus, the only variables are the vapor pressures and mass fractions. Although there are eight variables (vapor pressure and mass fraction for each of the four components), the following two constraints were used to simplify the process: (1) The initial vapor pressure of the second most volatile component, C2, was chosen to be approximately the same as that for TCP, 2.6×10^{-5} Pa. (We would expect their vapor pressures to be within a factor of 2 since they are similar in molecular weight—368 for TCP and 382 for C2—and from the same class of compounds.) (2) The initial vapor pressure of the mixture is greater than 1.0×10^{-4} Pa (based on the measured initial mass loss rate during the first 72 h). These conditions were used to “pin” the vapor pressures in approximately the correct range since the shape of the percent-loss curve in the model depends on the ratio of vapor pressures of the components, not the absolute values. The mass fractions were limited to the composition specifications for the product. [The composition as % (w/w) listed in order of decreasing volatility according to the manufacturer’s specification is the following: Triphenyl phosphate (C1), 25–30%; t-butylphenyldiphenyl phosphate (C2), 40–45%; di-(t-butylphenyl)phenyl phosphate (C3), 20–25%; and, tri-(t-butylphenyl) phosphate (C4), 2–5%.] In fitting the model to the experimental data, we took advantage of the fact that the vapor pressures and mole fractions of C1 and C2 were going to have the largest influence on the fit since only 60% of the additive had been lost in the experiment. As a result, the fit is essentially insensitive to the variables for C4, and only somewhat sensitive to those for C3.

In the program, each run is divided into 500 equal time intervals (points). (When normalized to the experimental data, each time interval corresponds to ~2.87 h.) For each point, the percent loss, total vapor pressure, and mole fraction distribution were calculated and stored. At the end of a run, we compared the shape and magnitude of the model percent loss vs time characteristics to the experimental data. The vapor pressures, composition, and a “time” constant were adjusted within the constraints listed above, and another run was initiated. The program takes only a few seconds to run, so the majority of the actual time involved is in comparing and plotting the data. The “shape” is relatively sensitive to the ratio of the vapor pressures at a fixed composition so that the number of possible combinations to give the appropriate fit are limited. The initial choice of the ratio of the vapor pressures was based on an assessment of the high-temperature vapor pressure data for various phosphate esters (1), which suggest that the vapor pressure decreases by a factor of 10 for each additional t-butyl group. The initial choice of vapor pressures does not affect the final calculated values; a poor initial choice only increases the number of iterative trials needed to obtain the final values..

3.2.2 Results

In Figure 6, the fit of the model to the experimental data is shown. The model is the solid line, and the experimental data for the four different samples are each given a different symbol. The fit to the data is excellent. The composition was: C1 – 30.1%, C2 – 40.4%, C3 – 24.9%, and C4 – 4.6%. The initial rate of the model fit in Figure 6 was used to calculate the initial experimentally determined vapor pressure of the mixture, assuming that the initial vapor pressure is dominated by the most volatile component, C1. The initial vapor pressure was calculated to be 1.1×10^{-4} Pa for the experimental

data, which satisfies our original constraint on the initial vapor pressure of the mixture. The individual component vapor pressures were calculated using this total vapor pressure, the ratios of the component vapor pressures from the model, and their initial mole fractions, also from the model. The component vapor pressures are given in Table 1 along with vapor pressures estimated by extrapolating data from high temperatures. As with the TCP and hydrocarbon mineral oil⁴ data, extrapolation of the high-temperature literature data gives values for the vapor pressures at lower temperatures that are considerably higher than the experimental and modeled data. Again, this is because the Clausius-Clapeyron relationship is curved concave downward over the large range of vapor pressures.

As mentioned previously, we have confidence in the magnitudes of the vapor pressure values obtained in this work since the shape of the curve in Figure 6 is very sensitive to the ratio of component vapor pressures. The early portions of the evaporation are affected by the vapor pressures of C1 and C2, and the slope at longer times is affected by the vapor pressure of C3. The vapor pressure of C4 is a rough estimate based on the values for the lower MW components. C4 is present in the smallest mole fraction in the mixture, and not much is lost during the experiment. Thus, its vapor pressure has the least influence on the shape of the curve. Only its mole fraction is critical since it influences the mole fractions of the more volatile components.

As was the case with the TCP additive, it was important to estimate the loss during the 24-h pump-down periods. Based on the initial vapor pressure and the fact that the Clausius-Clapeyron relationship is most likely steeper than predicted by the high-temperature data for the aryl phosphate esters, we estimate that during the first pump down, ≤ 0.1 mg was lost. For the subsequent pump-down periods, the loss would be less because the vapor pressure is decreasing with time. This small loss amount during pumpdown does not significantly affect the results.

Figure 7 shows the vapor pressure as a function of time from the model. The calculated vapor pressure decreases rapidly while the lighter components are evaporating, then assumes a much more shallow slope. Figure 8 shows the calculated mole fraction of each component as a function of time. C1 is essentially gone after 600 h. The mole fractions of C2, C3, and C4 increase due to the loss of C1. (C1 is more volatile so that it is lost at a faster rate than the other components, giving rise to an increase in the mole fractions of the other components. Of course, the total mass decreases with time.) After ~ 350 h, the mole fraction of C2 begins to decrease. At this point, the loss is essentially controlled by the vapor pressures of C2 and C3 since they are major components in the remaining oil.

Table 1. Vapor Pressures at 50°C for Aryl Phosphate Ester Mixture Components

Component	Chemical Name	Model VP (Pa)	Extrapol. Lit. VP (Pa)
C1	triphenyl phosphate	3.1×10^{-4}	1.7×10^{-1} (a)
			1.3×10^{-2} (b)
C2	t-butylphenyl diphenyl phosphate	2.1×10^{-5}	4.0×10^{-2} (a)
C3	di-(t-butylphenyl)phenyl phosphate	2.1×10^{-6}	7.0×10^{-3} (a)
C4	tri-(t-butylphenyl) phosphate	2.1×10^{-7}	8.6×10^{-4} (a)

a. Values derived by extrapolating high-temperature data from reference 1 using linear log vapor pressure vs molecular weight approximation.

b. Extrapolated from high-temperature data from reference 1.

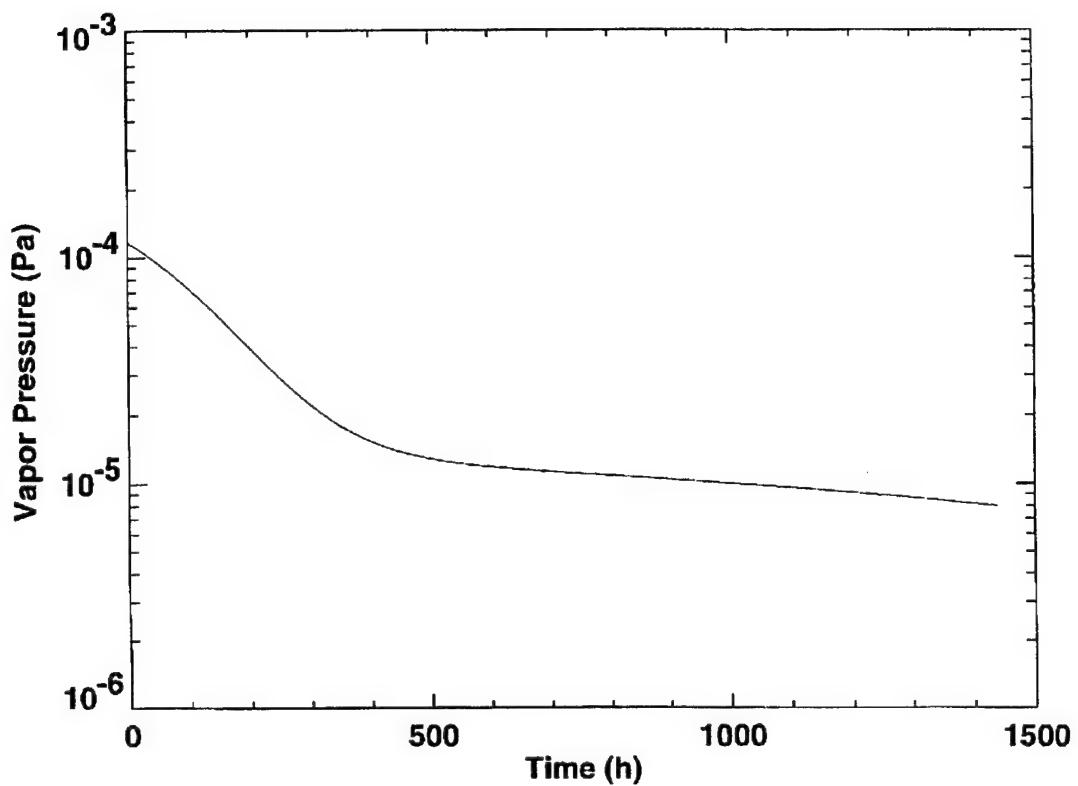


Figure 7. Aryl phosphate ester mixture vapor pressure vs time at 50°C.

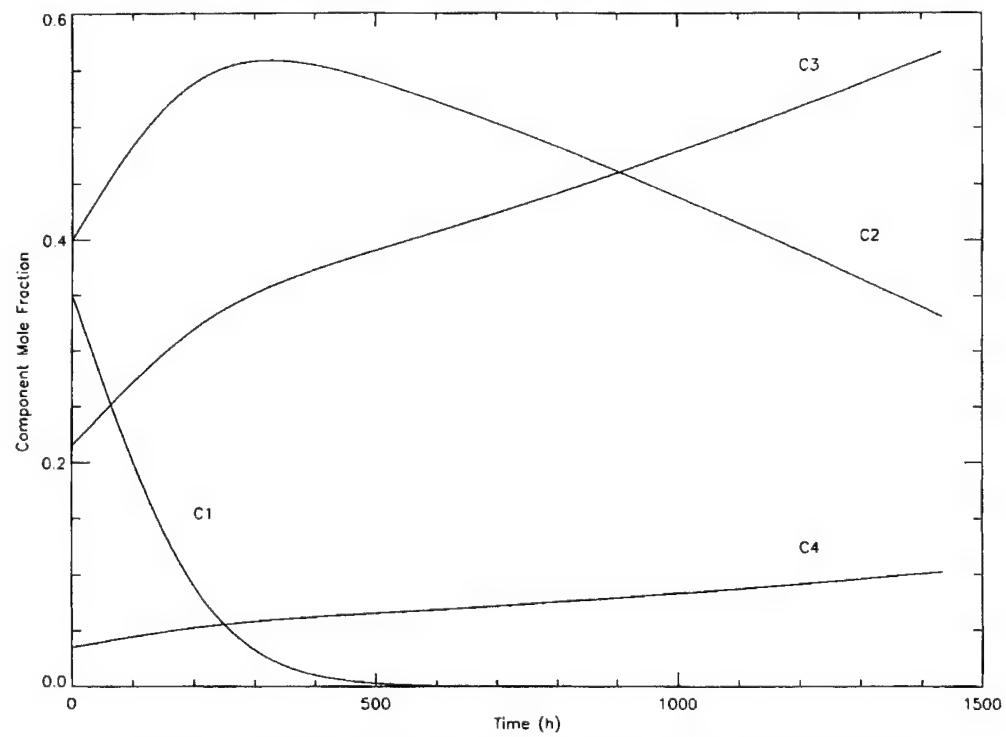


Figure 8. Aryl phosphate ester mixture component mole fractions vs time.

This is consistent with our earlier comment that the relative vapor pressures of these components are reasonably accurate. The C4 mole fraction increases throughout the run but remains a minor component.

3.2.3 Diffusion Considerations

In the model, it is assumed that the additive mixtures are mixed rapidly via diffusion on the time scale of the evaporation experiments. We can check this assumption by comparing the flux of material leaving via evaporation with the replacement flux of material being supplied by the bulk of the solution via diffusion. The initial loss flux for C1 can be calculated from the experimental data (see Figure 6): 7.5 mg of material leaving a surface of 0.8 cm^2 area in 100 h results in a flux of $0.09 \text{ mg cm}^{-2} \text{ h}^{-1}$. The replacement flux is given by

$$F = -D \frac{\partial C}{\partial x}, \quad (3)$$

where D is the diffusion coefficient, C is the concentration of C1, and x is the distance over which diffusion is taking place. D can be estimated as

$$D = \frac{RT}{6\pi\eta\sigma N_A}, \quad (4)$$

where R is the gas constant ($= 8.3 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1}$), T is the temperature in K, η is the viscosity in poise (about 0.54 poise for this material at 323 K), σ is the radius of the molecule in cm (about 10 Å), and N_A is Avogadro's number (6.02×10^{23}). D is about $4.4 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$. The concentration gradient can be approximated by assuming that the surface is totally depleted in C1, and that C1 reaches its nominal value (0.3 g cm^{-3}) only at the bottom of the solution (0.056 cm from the surface). This is an underestimate since the depletion will actually occur over a much smaller distance. However, using this assumption, we can calculate a lower bound for F to be $0.8 \text{ mg cm}^{-2} \text{ h}^{-1}$. The replacement is thus much faster than the loss, and the solution can be considered to be well mixed.

4. Conclusions

From the experimental evaporation data, we have determined the vapor pressures at 50°C of the components of an aryl phosphate ester additive mixture and TCP. Extrapolating high-temperature data over large ranges of temperature and vapor pressure (linear Clausius-Clapeyron behavior) results in calculated vapor pressures that are much larger than the values for aryl phosphate ester additives determined in our experiments. Generally, this leads to overestimating the rate of additive loss from spacecraft moving mechanical assemblies in the orbital environment. This is important because the additives actually remain in the bearings much longer, resulting in, potentially, longer system life than would have been predicted using extrapolated vapor pressure data.

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TECHNOLOGY OPERATIONS

The Aerospace Corporation functions as an "architect-engineer" for national security programs, specializing in advanced military space systems. The Corporation's Technology Operations supports the effective and timely development and operation of national security systems through scientific research and the application of advanced technology. Vital to the success of the Corporation is the technical staff's wide-ranging expertise and its ability to stay abreast of new technological developments and program support issues associated with rapidly evolving space systems. Contributing capabilities are provided by these individual Technology Centers:

Electronics Technology Center: Microelectronics, VLSI reliability, failure analysis, solid-state device physics, compound semiconductors, radiation effects, infrared and CCD detector devices, Micro-Electro-Mechanical Systems (MEMS), and data storage and display technologies; lasers and electro-optics, solid state laser design, micro-optics, optical communications, and fiber optic sensors; atomic frequency standards, applied laser spectroscopy, laser chemistry, atmospheric propagation and beam control, LIDAR/LADAR remote sensing; solar cell and array testing and evaluation, battery electrochemistry, battery testing and evaluation.

Mechanics and Materials Technology Center: Evaluation and characterization of new materials: metals, alloys, ceramics, polymers and composites; development and analysis of advanced materials processing and deposition techniques; nondestructive evaluation, component failure analysis and reliability; fracture mechanics and stress corrosion; analysis and evaluation of materials at cryogenic and elevated temperatures; launch vehicle fluid mechanics, heat transfer and flight dynamics; aerothermodynamics; chemical and electric propulsion; environmental chemistry; combustion processes; spacecraft structural mechanics, space environment effects on materials, hardening and vulnerability assessment; contamination, thermal and structural control; lubrication and surface phenomena; microengineering technology and microinstrument development.

Space and Environment Technology Center: Magnetospheric, auroral and cosmic ray physics, wave-particle interactions, magnetospheric plasma waves; atmospheric and ionospheric physics, density and composition of the upper atmosphere, remote sensing, hyperspectral imagery; solar physics, infrared astronomy, infrared signature analysis; effects of solar activity, magnetic storms and nuclear explosions on the earth's atmosphere, ionosphere and magnetosphere; effects of electromagnetic and particulate radiations on space systems; component testing, space instrumentation; environmental monitoring, trace detection; atmospheric chemical reactions, atmospheric optics, light scattering, state-specific chemical reactions and radiative signatures of missile plumes, and sensor out-of-field-of-view rejection.